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EFFECT OF PARTICLE FORM ON THE CONSTANT OF THE RATE OF COAGULATION OF AEROSOLS

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In a preceding work (1) we pointed out the effect of the form of particles on the stability of aerosols. It was there proposed that the change in form of the arborescent aggregates of particles in an electric field under the action of foreign vapors is caused by the change of form of the aerosol particles themselves, as a result of which the constant of the coagulation rate of the aerosols may have various numerical values.

The present work served to check the results obtained in the previous work on other systems, and it was intended as a study of the relation of the constant of the coagulation rate of the aerosols during transition of aerosol particles of leaf form into needle form, which most fully facilitates the transfer to aerosols of G. Müller's (2) theoretical conclusion on the coagulation of sols with particles of nonspherical form.

Experimental Results

We have previously described (1, 3) the method of obtaining aerosols and foreign vapors, and the methods of determining the weight concentration of aerosols, measuring aerosol particles, and carrying on ultramicroscopic researches and investigations of the form of particle aggregates in an electric field, which permit the growth of arborescent particle aggregates and their changes in form to be fixed under a microscope. (See appended abstract of bibliography item 3.)

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Aerosols of anthraquinone and nitrosodimethylaniline were chosen for investigation. The latter's particles in clear air take the form of leaves. An aerosol with such a particle form was of greatest interest for our investigations, since there was the possibility of the particle aggregates changing not only into spherical but also into needle form under the action of foreign vapors.

The investigation of the growth of arborescent aggregates and their formal changes in an electric field have shown that the form of the arborescent aggregates can become spherical only under the action of vapors of foreign substances which are solvents for the aerosol particles under the conditions given.

The form of arborescent aggregates of nitrosodimethylaniline tends to be spherical under the action of chloroform, ether, sulfuric acid, oleic acid, and phenol vapors (Figure 1, a, b [photograph, not reproduced]).

The form of arborescent aggregates of anthraquinone also tends to sphericity in the presence of toluene and sulphuric acid vapors.

Ultramicroscopic measurements of the coagulation rate of aerosols show a good correspondence with the results of studying the growth of arborescent aggregates and their changes in form.

Investigation of the coagulation rate of a nitrosodimethylaniline aerosol in chloroform, ether, sulphuric acid, oleic acid, and phenol vapors showed that the coagulation rate of the aerosol is diminished in the presence of these vapors (curve III, Figure 2). The constant of the coagulation rate of an aerosol, which determines the inclination of the line, approaches the value corresponding to Smolukhovskiy's theory in this case (Table 1).

Investigation of the coagulation rate of an anthraquinone aerosol in toluene vapors and sulphuric acid vapors also shows a reduction of the coagulation rate of the aerosol in the presence of these vapors (curve II, Figure 3); the constant of the coagulation rate approximates the theoretical value in this case as well (Table 1).

With the growth of nitrosodimethylaniline aerosol aggregates in an electric field in the presence of ammonia vapors, the formation of aggregates of arborescent form is also observed, but on the sides of these aggregates on the surface of the electrode, fine attenuated aggregates are formed in the shape of hooks. The formation of these aggregates points to the possibility of a change of arborescent aggregates to a longer form.

The study of the coagulation rate of a nitrosodimethylaniline aerosol in ammonia vapors has shown that in these cases the coagulation rate increases considerably with time (curve I, Figure 2) and the value of the constant of the coagulation rate is considerably increased (Table 1).

The weight concentration of aerosols in all the experiments was 25 mg per cu m. The average radius of the particles was about $3 \cdot 10^{-5}$ cm. The experiments were conducted at temperatures of 8 to 12 degrees C. The relative humidity of the air in the room and in the equipment did not exceed 30 percent. The buoyancy of the foreign vapors shifted from 10^{-3} mm to about that of saturated vapors.

In studying the growth and form of arborescent aggregates the following fact should be noted. In clear air, within an electric field, arborescent aggregates of a very different shape and size are formed, in relation to the physical and chemical properties of the substance from which the aerosol is

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formed. In the presence of the voltage of the electric field these arborescent aggregates are very stable, but without the voltage they disintegrate almost immediately. This is especially easy to observe in the case of arborescent aggregates formed from aerosols of ammonium chloride and stearic acid. The swift disintegration of arborescent aggregates in the absence of an electric field points to the absence of a stable bond between aerosol particles (4).

Evaluation of Results

The experimental data given here and also that obtained in the previous work (1) permits the conclusion that foreign vapors in the air can affect the coagulation rate of aerosols both positively and negatively. The mechanism and the causes remain to be explained.

It is of course possible to assume, as certain authors have done (5, 6, 7, 8, 9) that adsorption gas (vapor) films are formed on the surface of the aerosol particles from foreign vapors which are stably connected with the aerosol particles by sorption capacities and which can influence the effectiveness of the collision of the particles, which in its turn may lead to a reduction in the rate of aerosol coagulation. It favors this effect since it takes place in protected sols. It should be recognized that with the coagulation of anthraquinone and nitrosodimethylaniline aerosols in chloroform, ether, sulfuric acid, oleic acid, phenol, and toluene vapors not all particle collisions are effective, which contradicts the theory. The constant of the aerosol coagulation rate, obtained empirically, should in this case have had a numerical value less than the theoretical one, inasmuch as the foreign substance vapors can interfere with the effectiveness of the particle collisions. Actually, however, the data we obtained from the aerosols experimentally in vapors of various substances show a good correspondence with Smolukhovskiy's theory. The value of the coagulation-rate constant is close to the theoretical one, and the equation $\sigma_t = \sigma_0 e^{-\lambda t}$, where σ_0 is the initial particle volume, σ_t is the particle volume after the lapse of some time in the existence of the aerosol, t is the time, and λ is the coagulation-rate constant, remains correct throughout both series of experiments, conducted in the atmosphere as well as in the presence of foreign vapors.

The absence of a stable connection between gas (vapor) films and the aerosol particles conflicts with the argument for the effectiveness of adsorption films from foreign vapors upon the collision of particles. The known observations are in agreement with this opinion, when the aerosol particles do not come into contact with hard or liquid surfaces (10) due to their mechanical envelopment by the air.

Finally, the results of a series of experiments in which no effect of the films from foreign vapors upon the aerosol coagulation rate could be found (11, 12) were contrary to this proposition.

In our work (3) we did not observe any effects of phenol, oleic acid, glycerol, or water vapors upon the aerosol coagulation rate of stearic acid, paraffin, or mineral-oil aerosols. The increase we obtained in the coagulation rate of the nitrosodimethylaniline aerosol in ammonia vapors indicates the baselessness of such an assumption.

Thus, according to our experiments there are only two remaining factors from which changes could be expected in the aerosol coagulation rate of nitrosodimethylaniline: (1) change in the electric charge of aerosol particles, and (2) change of form of aerosol particles in the sorption of foreign vapors.

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It is well known that the electric properties of aerosols obtained at high and low temperatures are quite different (13). In our experiments aerosols were obtained at temperatures not exceeding 290 degrees C. We therefore investigated the coagulation of weakly charged aerosols, the particles of which might obtain charges of both signs in the course of the life of aerosols as a result of their adsorption of ions in the dispersion medium.

According to the data of Whitlow-Grey and Patterson in natural ionization, the number of charged aerosol particles in weakly charged aerosols may reach 70 percent in the course of time; but the authors did not succeed in these researches in discovering the effects of a common bipolar charge of aerosols upon their coagulation rate. N. Fuks, Petryanov, and others (14-20) have proved that only an intensive charge of an aerosol can lower its stability to any appreciable degree; a moderate bipolar charge has no effect, practically speaking, upon the stability of aerosols, and consequently no effect is noted upon their coagulation rate.

In the absence in the laboratory of radioactive and other materials which would produce an artificial charge in aerosols, the empirical data given above shows a good correspondence with Smolukhovskiy's theory; therefore, in our experiments it must be recognized that in the contacts of aerosol particles they adhere without regard to their charges.

As a result, the simple proposition remains that the change in form of the aerosol particles in their sorption of foreign vapors is the factor affecting the coagulation rate of aerosols and that it appeared as a positive and negative factor in the change of the coagulation rate of aerosols.

This explanation of the results obtained is based upon the assumption that the change of form of the particle aggregates under the action of foreign vapors is caused by changes of form of the same aerosol particles, as a result of which the constant of the aerosol coagulation rate may have various numerical values.

This assumption is not in contradiction with the theory, and the experimental data obtained qualitatively and quantitatively supports the function of the change of form of the aerosol particles in agreement with the assumed relationship.

Actually, in the absence of foreign bodies in the electric field, aggregates of arborescent form appear on the lines of force, due to the small aperture in the center of the electrode. The determined coagulation rate of aerosols (curve I, Figure 2; curve I, Figure 3).

In the presence of aerosols of chloroform, ether, sulphuric acid, oleic acid, phenol, and toluene vapors well adsorbed by particles, aggregates less than the preceding in height are formed in the electric field and a larger amount of deposited aerosol particles is observed at the base of the aggregates, which is an indication that here the arborescent aggregates tend toward an isodimensional form. In these cases, in some part of the aerosol particles having a minimum radius, the structure of the crystals on the surface is weakened to a point where the particles can no longer be joined together and held in space.

Weakening of the crystalline structure of the particles in all probability leads to leveling of the most acute angles on the surface of the particles, as a result of which a decrease in the aerosol coagulation rate is noted (curve III, Figure 2; curve II, Figure 3). The decrease of the numerical value of the constant of the aerosol coagulation rate and the approach of its magnitude to a value consistent with Smolukhovskiy's theory

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clearly indicate that in those cases the aerosol particles in the sorption of foreign vapors tend toward a spherical form.

The mechanism of the action of foreign vapors upon aerosol particles in case of a change of anisodimensional particles into spherical ones probably amounts to leveling of the most acute angles of the surface of the particles, due to weakening of its crystalline structure.

In studying the changes in nitrosodimethylaniline particle aggregates in the presence of ammonia vapors in the center of an electric field, the same formation of arborescent aggregates is to be observed. At the sides of these aggregates on the surface of the electrode, where the lines of force are less curved, fine aggregates are formed suggesting the form of hooks. The very fact of the formation, under the action of an electric field, of aggregates in the shape of thin hooks shows that in this case the form of arborescent aggregates under the influence of ammonia vapors tends to be anisodimensional.

Actually, as ultramicroscopic researches have shown, there is to be observed here a significant increase in the aerosol coagulation rate (curve 1, Figure 2). The constant of the aerosol coagulation rate of nitrosodimethylaniline in this case is increased by two and a half times in comparison with its theoretical value (Table 1).

The increase in the aerosol coagulation rate in ammonia vapors is also to be explained by Muller's (2) theory, which specifies that the coagulation of particles of nonspherical form always proceeds faster than the coagulation of spherical particles. It follows from this that in the coagulation of the nitrosodimethylaniline aerosol in the presence of ammonia vapors the form of the aerosol particles changes from discs to needle-like shapes. This agrees closely with the investigations of aggregates in an electric field.

The problem of the mechanism of change in form of aerosol particles requires further investigation. However, we may assume that the increase in the coagulation rate of the nitrosodimethylaniline aerosol in the presence of ammonia vapors is caused by the formation of needlelike crystals on the surface of the particles, which also tends to increase the radius of their sphere of influence.

On the basis of the experimental results obtained we may assert that the transition of aerosol particles from the form of rods to spheres, as well as the change from discoid (leaflets) to needle form under the influence of foreign vapors clearly shows the relationship of the coagulation-rate constant to the form of the aerosol particles.

At this point it would probably be appropriate to interpret the results obtained by L. V. Radushkevich (21), who obtained a change of the constant of the aerosol coagulation rate of ammonium chloride from $0.26 \cdot 10^{-7}$ cc/minute to $0.54 \cdot 10^{-7}$ cc/minute. In his experiments the humidity in the room in which the aerosols were formed, unfortunately, was not regulated and recorded. Undoubtedly, over the period of his experiments, which were continued for more than a month, the relative humidity in the room varied to a considerable degree, and as a result the author obtained an ammonium chloride aerosol with a different form of particles of different effective radius, which produced different numerical values for the aerosol-coagulation-rate constant.

The same observation probably applies to the experiments of the English authors Whitelaw-Grey and Patterson (22), who obtained values for the constant of the aerosol coagulation rate of ammonium chloride from $0.31 \cdot 10^{-7}$ to $0.47 \cdot 10^{-7}$ cc/minute.

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Our experiments have shown that in studying the coagulation of aerosols with anisodimensional particles, the form of the particle must be considered. In these cases, in Smolukhovskiy's constant of the coagulation rate, in addition to the corrections for the polydispersion of the aerosol and for the mobility of the particles, a correction must also be made for the form of the particles. This correction obviously cannot be overlooked, as in some cases it can increase the numerical value of the constant of the aerosol coagulation rate by 250 percent.

In conclusion, I wish to convey my deep appreciation to Corresponding Member of the Academy of Sciences of the USSR B. V. Deryagin for his valuable advice and discussion of results.

Conclusions

1. The relation of the constant of the aerosol coagulation rate to the form of the aerosol particles is established. With the change of particles of discoid form (leaflets) to a needlelike form the constant of the aerosol coagulation rate increases in accordance with Myuller's theory of the coagulation of sols with particles of nonspherical form. When the aerosol particles assume a spherical form, the constant of the aerosol coagulation rate decreases and approaches a value consistent with Smolukhovskiy's theory.

2. The obtained relation of the constant of the aerosol coagulation rate to the form of the particles explains these experimental data, when with a single weight concentration of the aerosol and the same radius of the particles, different numerical values are obtained for the constant of the aerosol coagulation rate.

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[Appended figures follow]

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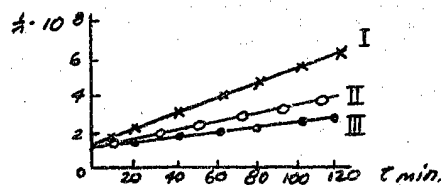


Figure 2. Nitrosodimethylaniline Coagulation Curves

The time in minutes is plotted on the axis of the abscissae and the particle volumes on the axis of the ordinates. Curve I is in NH_3 vapor, curve II in the absence of foreign vapors, and curve III in CHCl_3 , $\text{C}_4\text{H}_{10}\text{O}$, H_2SO_4 , $\text{C}_6\text{H}_5\text{Cl}$, and $\text{C}_{17}\text{H}_{35}\text{COOH}$ vapors.

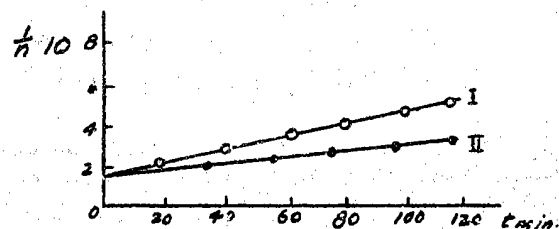


Figure 3. Anthraquinone Coagulation Curves

The time in minutes is plotted on the axis of the abscissae and the particle volumes on the axis of the ordinates. Curve I is in the absence of foreign vapors, and curve II is in C_7H_8 and H_2SO_4 vapors.

Table 1. The Constant (K) of the Aerosol Coagulation Rate

(In cubic centimeters per minute)

	<u>Nitrosodimethylaniline</u>	<u>Anthraquinone</u>
In Air	0.27×10^{-7}	0.30×10^{-7}
In Chloroform, Ether Sulfuric Acid, Oleic Acid, and Phenol Vapors	0.20×10^{-7}	--
In Ammonia Vapor	0.48×10^{-7}	--
In Toluene and Sulfuric Acid Vapors	--	0.203×10^{-7}
Calculated by the Formula	0.199×10^{-7}	0.199×10^{-7}

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NOTE: The values of K were calculated by the formula,

$$\frac{2RT\zeta}{3\eta N} \left(1 + \frac{\lambda}{r}\right)$$

where R is the gas constant, T is the absolute temperature, η is the viscosity of the dispersion medium, N is Avogadro's number, λ is the constant, λ is the average length of the path of the gas molecule, and r is the radius of the particles.

APPENDIX

I. G. Artemov, "Effect of Foreign Vapors on the Coagulation of Aerosols," Zh. Fiz. Khim., Vol XX, 1946, pp 553-560

Abstract

Foreign vapors have no effect on the rate of coagulation. Contrary data in the literature are due to errors of technique. Mists of mineral oil, stearic acid, and purified paraffin were produced by cooling the corresponding vapors. Their average particle radius was 10^{-5} cm, and the concentration was 25 mg/cu m. The progress of coagulation was followed by counting the particles in dark-field illumination. No measurable sedimentation took place during the experiments, which were extended for up to 3 hours. The change in the particle number, n, was produced solely by the formation of larger particles from several small ones. The magnitude of n increased linearly with the time, t (e.g., in the ratio of 4:1 when t rose from 20 to 100 minutes). The rate of increase depended very little on the substance dispersed and was not affected by vapors of phenol, oleic acid, glycerol, and water. The concentration of the vapor in the mist was varied from 0.5 mg/cu m almost to saturation. The alleged proofs for the existence of thick "adsorption" layers on aerosol particles are adversely criticized.

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